Evaluated Kinetics of Terminal and Non-Terminal Addition of Hydrogen Atoms to 1-Alkenes: A Shock Tube Study of H + 1-Butene

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Supporting Information

ABSTRACT: Single-pulse shock tube methods have been used to thermally generate hydrogen atoms and investigate the kinetics of their addition reactions with 1-butene at temperatures of 880 to 1120 K and pressures of 145 to 245 kPa. Rate parameters for the unimolecular decomposition of 1-butene are also reported. Addition of H atoms to the π bond of 1-butene results in displacement of either methyl or ethyl depending on whether addition occurs at the terminal or nonterminal position. Postshock monitoring of the initial alkene products has been used to determine the relative and absolute reaction rates. Absolute rate constants have been derived relative to the reference reaction of displacement of methyl from 1,3,5-trimethylbenzene (135TMB). With $k(H + 135TMB \rightarrow m$ -xylene + CH_3) = $6.7 \times 10^{13} \exp(-3255/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, we find the following: $k(H + 1\text{-butene} \rightarrow \text{propene} + CH_3) = k_{10} = 3.93 \times 10^{13} \exp(-1152 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, [880–1120 K; 145–245 kPa]; $k_{10}/k_{11} = 10^{(0.058\pm0.059)} \exp[(818 \pm 141) \text{ K/T})$, 971–1120 K. Uncertainties (2σ) in the absolute rate constants are about a factor of 1.5,



while the relative rate constants should be accurate to within $\pm 15\%$. The displacement rate constants are shown to be very close to the high pressure limiting rate constants for addition of H, and the present measurements are the first direct determination of the branching ratio for 1-olefins at high temperatures. At 1000 K, addition to the terminal site is favored over the nonterminal position by a factor of 2.59 ± 0.39 , where the uncertainty is 2σ and includes possible systematic errors. Combining the present results with evaluated data from the literature pertaining to temperatures of <440 K leads us to recommend the following: k_{∞} (H + 1-butene $\rightarrow 2$ -butyl) = $1.05 \times 10^9 T^{1.40} \exp(-366/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, [220-2000 K]; k_{∞} (H + 1-butene $\rightarrow 1$ -butyl) = $9.02 \times 10^8 T^{1.40} \exp(-1162/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, [220-2000 K]; k_{∞} (H + 1-olefins should be very similar. Despite this, a factor of three discrepancy in the branching ratio for terminal and nonterminal addition is noted when comparing the present values with recommendations from a recent model of the important H + propene reaction. This difference is suggested to be well outside of the possible experimental errors of the present study or the expected differences with 1-butene. There thus appear to be inconsistencies in the current model for propene. In particular the addition branching ratio from that model should not be used as a reference value in extrapolations to other systems via rate rules or automated mechanism generation techniques.

1. INTRODUCTION

Hydrogen atoms are active radicals in the combustion and pyrolysis of fuels. Addition of H to the π bonds of unsaturated compounds present or created in such systems leads to unstable intermediates that rapidly fragment at high temperatures. In unsymmetrical olefins, product ratios are strongly influenced by relative rates of addition to the alternate ends of the unsaturated center. Because the pattern of fragmentation products will propagate through the subsequent chemistry of the system, the relative addition rates are often of greater importance than the absolute rate constants in determining system behavior. Consequently, these are important parameters in the development of reliable detailed chemical kinetic models. Through detailed balance, the kinetics apply equally to the reverse radical decompositions, which are also reactions of great interest.

The present paper is concerned with the relative and absolute rate constants near 1000 K for addition of H atoms to

the terminal and nonterminal positions of 1-butene. As a prototypical 1-olefin, information on this species is representative of this entire class of compounds. Accurate data on 1olefins are of particular interest as at high temperatures such species are a primary decomposition product of all unbranched alkyl radicals, which represent major constituents in the conversion pathways of almost all hydrocarbon fuel mixtures in use today.

There exists a considerable body of work on rates of hydrogen atom addition to olefins at temperatures much lower than those considered here. Reviews and compilations are available in $book^{1,2}$ and electronic database forms.³ Most studies have measured only the overall rate constant with no direct information on the site of addition. Nonetheless, for the

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normal 1-olefins near ambient temperatures, on the basis of secondary products formed from the adduct radicals, it has been inferred^{1,4–7} that addition to the terminal position is 15-20 times faster than to the nonterminal site. This is in general agreement with recent computational studies on the addition of H to propene.⁸ At high temperatures there are no direct measurements of the branching ratio for terminal and nonterminal addition, and there remains significant uncertainty in the extrapolation of the low temperature results. For instance, under combustion-relevant conditions, the branching ratio setimated by Curran in his 2006 review⁹ are significantly different from the 2013 values of Miller and Klippenstein.⁸

Addition of H to olefins leads to alkyl radicals. If an alkyl group, R, is attached to the carbon adjacent to the resulting radical center, beta scission of the weak C-C bond is much faster than re-ejection of H via C-H bond scission. At high temperatures the net reaction is the rapid displacement of R:

$$H + RCH = CH_2 \rightarrow RCH_2 - CH_2 \rightarrow R + CH_2 = CH_2$$
(R1)

Near 1000 K, our recent experimental work,^{10,11} and that of others,¹² as well as computational studies,⁸ show that the branching fraction for C–H scission is small, generally in the range 0.01–0.05. Thus, in the absence of other reactions, rates of displacement of R correspond closely with rates of H addition. An important process in C5 and larger systems is the competing isomerization of the radical via internal H transfer reactions,^{10,13–16} but this complication is not significant for the C4 species considered in the present work.

In the current study, we utilize shock tube methods to create small concentrations of H atoms in the presence of excess 1butene, the substrate under consideration. Short reaction times and dilute conditions enable us to isolate the initial reactions, and the products of terminal and nonterminal addition are distinct and quantitatively produced, allowing the determination of the relative kinetics on the basis of observed products. Absolute values are derived relative to a reference reaction. In previous investigations we have determined rates corresponding to nonterminal H addition for a number of alkenes at temperatures near 1000 K.^{11,17,18} While the precise degree of variation within the hydrocarbon class remains to be established, our data show that rate constants for H addition vary only slightly with the chain length of the alkene. This result is consistent with thermochemical kinetics¹⁹ and with the studies at low temperatures.¹⁻³ As justified later in more detail, it also suggests that the present work on 1-butene can be utilized as a standard reference, and that the results should be transferrable to other unbranched 1-alkenes with minimal errors.

2. EXPERIMENTAL METHODS

Shock Tube Methodology. Shock tubes are ideal for the isolation of gas phase processes at high temperatures because of the rapid heating, short time scale of the experiments, and the absence of interactions with hot surfaces on which interfering reactions can occur. It is the only well-developed technique with these characteristics. The present measurements are carried out in a single pulse shock tube apparatus that is heated throughout to typically 373 K, and configured so as to have reaction times of $(500 \pm 50) \ \mu s$, as determined by high speed pressure transducers. Details of the instrument have been reported elsewhere.^{20,21} Experiments are conducted in an argon bath gas and involve the creation of small quantities [<50 μ L/L

(ppm)] of hydrogen atoms in the presence of a large excess [typically 10000 μ L/L] of 1-butene, the substrate of interest, and 1,3,5-trimethylbenzene (135TMB). The latter component serves as both a radical chain inhibitor and a rate reference (*vide infra*) through the methyl displacement reaction that occurs via attack of H atoms on 135TMB.

In our experiments, shock temperatures are determined by following a standard unimolecular reaction that has well-defined rate parameters. Experimental rate constants are determined utilizing

$$k_{\rm std} = \tau^{-1} \ln([\rm std]_i / [\rm std]_f)]$$

where τ is the reaction time and the subscripts *i* and *f* refer to the initial and final concentrations, respectively. The rate expression for the standard, $k_{\text{std}} = A \exp(-E/T)$, is easily rearranged to obtain the temperature of a particular experiment.

In the current experiments, at temperatures up to about 1030 K we use the unimolecular decomposition of chlorocyclopentane (CCP) as the temperature standard, taking the rate expression

k(chlorocyclopentane \rightarrow cyclopentene + HCl)/s⁻¹

$$= 4.47 \times 10^{13} \exp(-24570/T)$$

from our recent examination of several temperature standards.²¹ At temperatures higher than this, where CCP decomposition is too fast to function as a good standard, we use the decomposition of hexamethylethane (HME), the H atom precursor, as the temperature standard, using the rate expression k(hexamethylethane $\rightarrow 2 \ tert$ -butyl)/s⁻¹ = 2.51 × 10¹⁶ exp(-34400/T) s⁻¹ from the work of Tsang.^{22,23} In the midtemperature region, where both reactions could be utilized, the two standards gave equal temperatures within typically 5 K, with no apparent systematic differences. We estimate that the standard uncertainty (1 σ) in the derived absolute shock temperatures is about 1% under the conditions of the present work.^{21,22}

Most of the described experiments make use of the thermal decomposition of hexamethylethane (HME) as a convenient and well-studied source of hydrogen atoms. The reactions are

hexamethylethane $\rightarrow 2 tert$ -butyl (R2)

$$tert$$
-butyl \rightarrow isobutene + H (R3)

The initial bond fission in HME (R2) is the rate limiting step, with radical decomposition (R3) requiring a few microseconds or less under our conditions. Rate parameters are such that HME is only partially decomposed and the H atoms are generated over the full 500 μ s shock-heated time period. HME decomposition results in a stable coproduct, isobutene, that provides a direct count of the H atoms released into the system by the precursor. Product concentrations can thus be used to gauge the complexity of the secondary chemistry.

While HME decomposition is a rather clean source of H atoms, Tsang has reported²³ the formation of propene as a minor side process, corresponding to 3% of isobutene formation. In agreement with his observations, we find propene/isobutene product ratios of (0.035 ± 0.007) from separate experiments with mixtures containing only HME, inhibitor, and argon. In the current work, the propene yield attributed to attack of H on 1-butene was thus reduced by an amount equal to 0.035[isobutene], leading to an adjustment of typically 2–6%.

One additional set of experiments was carried out using ethyl iodide as the H atom source. This compound forms H atoms after fission of the weak C–I bond:

$$C_2H_5I \to C_2H_5 + I \tag{R4}$$

$$C_2H_5 \to C_2H_4 + H \tag{R5}$$

Molecular elimination of HI, eq R6, competes with fission of the C-I bond.

$$C_2H_5I \rightarrow C_2H_4 + HI \tag{R6}$$

Ethene is the olefin product in both cases so we cannot directly distinguish between the two mechanisms. However, based on our studies of other primary iodides,¹⁰ the C–I bond scission channel that leads to H atoms is expected to account for about 75% of reaction under our conditions. This is consistent with other studies of the reaction.^{24–28} The exact ratio does not impact the rate measurements and so is unimportant for our purposes: the feature of interest is that ethyl iodide decomposes more rapidly than HME, allowing the production of H atoms at lower temperatures. A disadvantage of this source, however, is that it produces ethene as a coproduct, compromising our ability to monitor the ethene-producing channel in the H + butene reaction.

Our experiments involve the generation of H atoms under conditions where 1-butene itself is largely stable. A small degree of unimolecular decomposition was suggested by some observed products, however, and we therefore undertook an ancillary study of 1-butene pyrolysis. In this latter work, conducted at temperatures higher than used in the H atom studies, we use the decomposition of *tert*-butyl alcohol as the temperature standard. This compound undergoes molecular elimination of water and the isobutene product is stable and can be used to monitor the reaction.

tert-butyl alcohol
$$\rightarrow$$
 isobutene + H₂O (R7)

A number of investigations of tert-butyl alcohol decomposition have been reported,³ including two comparative rate shock tube studies^{29,30} that lead to rate parameters versus the decomposition of cyclohexene, cyclohexene \rightarrow 1,3-butadiene + ethene, the rate of which is linked to the other temperature standards used by us. In the course of our work, however, we noted a number of inconsistencies in the previous reports of tert-butyl alcohol decomposition and this led us to carry out our own comparative rate study versus cyclohexene. We utilized mixtures containing (100 to 200) μ L/L of the substrates in the presence of about 10000 μ L/L of 135TMB as an inhibitor. These substrate concentrations are a factor of 10 to 50 lower than used in the previous comparative rate studies, thus better minimizing secondary chemistry, and this may account for some of the differences with previous works. A more complete account will be published elsewhere, but some of the key findings are noted here. First, when using the same reference rate constant for cyclohexene, the rate constants reported by Newman et al.³⁰ are more than a factor of 2 larger than those of Lewis et al.²⁹ Our own values are in much better accord with those of Lewis et al. Second, we find that at the higher temperatures of interest in the present work, C-C bond fission begins to compete with molecular elimination of water, and leads to acetone as a second stable product.

tert-butyl alcohol
$$\rightarrow$$
 (CH₃)₂COH + CH₃ (R8)

$$(CH_3)_2COH \rightarrow acetone + H (fast)$$
 (R9)

It is necessary to take C–C bond fission into account to derive accurate rate constants at higher temperatures. When using our preferred rate parameters for cyclohexene decomposition,²¹ k(cyclohexene \rightarrow 1,3-butadiene + ethene)/s⁻¹ = 1.41 × 10¹⁵ exp(-33500/T), we find the following:

270-300 kPa)

Adjusted to a common reference rate, our rate constants for the isobutene channel are about 20% smaller in the temperature region of overlap than those reported by Lewis et al., whose study covered 920 to 1175 K. Lewis et al. did not report acetone as a product, although this channel would be of less importance under most of their conditions. We find acetone production via the eq R8, eq R9 sequence to account for about 20% of reaction at our temperatures and pressures. Our activation energy for decomposition is slightly larger than that reported by Lewis et al., which is consistent with the higher energy bond fission channel becoming active at higher temperatures. Differences in the parameters may also reflect pressure effects and uncertainties due to the short temperature range covered in our study. We have used our own parameters as given above to derive temperatures in our study of 1-butene decomposition. Note that the listed values are specific to our conditions. They likely do not reflect high pressure limiting values and we do not recommend direct extrapolation outside of the studied conditions.

Gas Chromatographic-Mass Spectral Analyses. The present analyses utilized a Hewlett-Packard 6890N GC equipped with two columns and both flame ionization (FID) and mass spectral (MS) detectors. A few seconds after the shock, samples of the shocked gas are extracted into a preevacuated valve and loop system from a port located 5 cm from the end wall of shock tube. The neat sample is compressed to a pressure of 1 bar and the contents of two 1 mL sample loops are injected onto the GC columns, typically within about 60 s of the shock. A Restek 30 m × 0.53 mm i.d. Rt-alumina (aluminum oxide porous layer) capillary column was utilized for optimized detection of the lighter gases (typically smaller than C5). Larger species were separated on a J & W Scientific $30 \text{ m} \times 0.53 \text{ mm}$ i.d. DB-1 (100% dimethypolysiloxane) capillary column. Effluent from the DB-1 column was quantitatively split with an Agilent Technologies microfluidic splitter (Dean's Switch) and simultaneously sent to MS and FID detectors. Concentrations are based on the FID analyses, with the MS used primarily to confirm product identities. The GC oven is initially cooled with chilled nitrogen gas, and analyses are carried out using a ramped temperature program spanning 213-453 K (-60 to +180 °C) with constant carrier gas flow. Many of the lighter components are separated on both

columns, leading to duplicate analyses of these species. Results agreed typically within a few percent in such cases.

Molar FID responses of the C1–C5 olefins were determined from standard samples. Including possible systematic errors, we estimate the analytical uncertainty (1σ) for the main C1–C3 products to be about 3%. We lacked samples of many of the minor recombination products and absolute uncertainties for these compounds are estimated to be about twice as large, increasing to about 12% near the limits of detection, typically about 0.01 μ L/L.

Chemicals. 1-Butene (99+ %, Sigma-Aldrich), hexamethylethane (98%, Sigma-Aldrich), ethyl iodide (99%, Sigma-Aldrich), chlorocyclopentane (99%, Sigma-Aldrich), 1,3,5trimethylbenzene (135TMB, 99%, Aldrich), and argon (Praxair, 99.999%), were the chemicals used in the kinetic studies. 135TMB was redistilled to reduce a small background of *m*xylene; all other chemicals were used without further purification, other than degassing of liquids by standard freeze, pump, thaw techniques during preparation of the mixtures. GC analyses showed the main impurities in our sample of 1-butene to be 0.15% of butane and 0.004% of propane. At still lower levels were other trace hydrocarbon impurities, including methane, propene, 2-butenes, and 1,3-butadiene. Product amounts were corrected for any trace backgrounds, but none were present in quantities expected to impact the results.

3. RESULTS

Overview. The basis of the current study is to create a small concentration of hydrogen atoms in the presence of a large excess of 1-butene. Addition of H to the substrate results in radical intermediates that rapidly and quantitatively decompose to different stable products depending on the site of attack. The use of a radical inhibitor and an extremely dilute environment leads to conditions where the stable products do not react further and there is a one-to-one correspondence between observed products and the initial reactions of interest. This leads to accurate branching ratios. Absolute rate constants are derived relative to a competing reference reaction of H atoms with 135TMB.

The gas mixtures used are listed in Table 1. The majority of the work was carried out with HME as the H atom precursor, but ethyl iodide was used as the precursor in one set of experiments in order to obtain data at temperatures lower than possible with HME. Analysis of the initial data from the HMEcontaining mixtures indicated a small amount of direct

 Table 1. Gas Mixtures Used in the Present Experiments,

 Where the Remaining Balance Is Argon

	components in mixtures $(\mu L/L)^a$					
mixture	1-butene	135TMB	HME^{b}	$C_2H_5I^b$	CCP^{c}	<i>t</i> -BuOH ^c
А	3500	4640	53.7	-	75.0	_
В	4710	2880	93.8	-	70.9	-
С	4890	3010	40.4	-	73.0	-
D	2700	3990	-	88.2	53.3	-
Е	1020	3800	35.9	-	58.8	_
F	79.0	6300	-	_	-	52.7

"Numbers are the measured values. Standard uncertainties (1σ) in the absolute amounts are estimated as 3%. 135TMB = 1,3,5-trimethylbenzene, HME = hexamethylethane; C_2H_5I = ethyl iodide, CCP = chlorocyclopentane; *t*-BuOH = *tert*-butyl alcohol. ^bH atom precursor. ^cTemperature standard.

unimolecular decomposition of 1-butene at higher temperatures. Some additional pyrolysis experiments were therefore carried out to better define the stability of this compound. As a general test for systematic effects, we have varied the concentration of 1-butene by a factor of about five in the HME studies. Similarly, the ratio of the substrate to inhibitor (which also serves as the rate reference) was varied by a factor of about 6. As discussed below, the kinetic results from all mixtures were consistent and suggest that the chemistry of interest has been isolated.

Product Distribution and Mechanism. Isobutene and cyclopentene are the respective olefin products from the decomposition of our H atom precursor, HME, and temperature standard, chlorocyclopentene. Other observed hydrocarbons are ascribed as products of the reacting mixture of H atoms, 1-butene, and 135TMB inhibitor. Results are qualitatively similar for all mixtures. Selected product data from Mixture A are summarized in Figure 1, which shows



Figure 1. Distribution of selected products from mixture A. Results for other mixtures are qualitatively similar. 1,5-HDE = 1,5-hexadiene; 1,3-BDE = 1,3-butadiene; the recombination products of methyl and allyl radicals with 1,3-dimethylbenzyl (DMB) are respectively designated as $(CH_3 + DMB)$ and (allyl + DMB).

product amounts expressed as molar ratios relative to ethene formation. In the Supporting Information we tabulate for mixtures A through E the data on all products present at levels >1% of ethene. The main three products are methane, propene and ethene. In addition, at levels greater than 10% of ethene are found 1,3-butadiene, *m*-xylene, ethane, 1,5-hexadiene, 3,5-dimethylethylbenzene, and 3,5-dimethyl-(3-butenyl)benzene. At levels between 1% and 10% of ethene are ethyne, allene, propane, *E*-2-butene, *Z*-2-butene, *E*-2-pentene, *Z*-2-pentene, 3-methyl-1-butene, and 1,5-heptadiene. The high sensitivity of GC/MS analysis allowed the tentative identification of a few other components at still lower levels. These latter species were consistent with radical chemistry of trace hydrocarbon species, and amounts were insufficient to affect our results; they are not discussed here.

Chemistry Involving 1-Butene. The products listed above can be attributed to three initial reaction channels involving 1-butene, together with cross reactions arising from the chemistry of the 135TMB inhibitor. The primary reaction paths of 1-butene are postulated to involve addition of H atoms to 1-

butene, abstraction of H from 1-butene, and unimolecular dissociation of 1-butene.

Propene and ethene are by far the dominant olefin products and are the alkenes expected from terminal and nonterminal addition of H atoms to 1-butene, leading to displacement of methyl or ethyl:

$$H + 1$$
-butene $\rightarrow 2$ -butyl $\rightarrow propene + CH_3$ (R10)

H + 1-butene $\rightarrow 1$ -butyl \rightarrow ethene + ethyl (R11)

$$ethyl \rightarrow ethene + H$$
 (R12)

The intermediate butyl radicals are initially chemically activated, but the overall process may involve both activated and thermalized species. Note that the ethyl radicals produced in eq R11 will mainly eject H (reaction R12) at the high temperatures and dilute conditions of the present studies, so the expected net process for nonterminal addition is H + 1-butene \rightarrow 2 ethene + H.

Small amounts of E-2-butene and Z-2-butene are also observed. One way these can arise is by ejection of H from the 2-butyl radicals that are formed by terminal addition of H to 1-butene:

$$H + 1$$
-butene $\rightarrow 2$ -butyl $\rightarrow E$ -2-butene + H (R13)

$$H + 1$$
-butene $\rightarrow 2$ -butyl $\rightarrow Z$ -2-butene + H (R14)

There is presumably an analogous channel leading back to 1butene + H, but we are experimentally blind to that process. A second route to 2-butenes is discussed below, and is in fact postulated to be the dominant path, but formation of 2-butene is in any case a minor channel, with the summed isomers amounting to about 8% of propene.

Chemistry associated with abstraction of H from 1-butene and decomposition of the resulting intermediates is indicated in reactions R15-R21 as shown in Scheme 1. The abstracting

Scheme 1. Main Postulated Product Pathways Associated with Abstraction of H from 1-Butene and Subsequent Decomposition of the Radical Intermediates



radicals, X, are undefined, but will be predominantly H atoms and methyl radicals. The allylic hydrogens of 1-butene are expected to be much more reactive than the primary hydrogens, so the chemistry will channel mainly through the 1-methylallyl radical. This species is stabilized by the allylic resonance energy, but can undergo β -C–H scission to give 1,3-butadiene (see Scheme 1), which is an observed product (Figure 1). As shown below, 1-methylallyl may also recombine with H atoms, abstract H from the inhibitor or other species (RH), or disproportionate with H donating radicals (RH $^{\bullet}$) in the system. These reactions all lead to 1-butene or 2-butene.

H + 1-methylallyl $\rightarrow 1$ -butene (R22)

H + 1-methylallyl $\rightarrow 2$ -butene (*E* and *Z* isomers) (R23)

RH + 1-methylallyl $\rightarrow R + 1$ -butene (R24)

RH + 1-methylallyl $\rightarrow R + 2$ -butene (*E* and *Z* isomers) (R25)

$$RH^{\bullet} + 1$$
-methylallyl $\rightarrow R + 1$ -butene (R26)

$$RH^{\bullet} + 1$$
-methylallyl $\rightarrow R + 2$ -butene (*E* and *Z* isomers)
(R27)

With respect to the importance of the above reactions in formation of 2-butenes, we are able to draw some conclusions in conjunction with the results of our recent investigation³¹ of the kinetics of H abstraction from *n*-butane by H atoms and methyl radicals. In the studied *n*-butane systems, H abstraction processes lead to 2-butyl radicals, and hence to the same competition between formation of propene via ejection of methyl (R10) and formation of 2-butenes via eqs R13 and R14. Methylallyl radicals are not present in that system and modeling indicates that disproportionation of 2-butyl is minor because of its short lifetime. In those studies we can therefore ascribe 2-butene formation to eqs R13 and R14. Those data show 2-butene/propene ratios that are about one third of the values observed in the present experiments. This leads us to conclude that about two thirds of the 2-butenes observed in the present system arise from the above methylallyl chemistry, rather than unimolecular decomposition of 2-butyl radicals.

Abstraction of a primary H from 1-butene leads to but-3-en-1-yl. As indicated in Scheme 1, the subsequent decomposition of this species results in a distribution of 1,3-butadiene, ethene, and ethyne as stable products. Computational studies in the literature, $^{32-35}$ as well as calculations performed by us in the course of this work, suggest that formation of 1,3-butadiene is the dominant channel. This is consistent with our observation of only very minor amounts of ethyne in the product spectrum (Figure 1).

Some indication of the relative importance of abstraction and addition channels can be obtained by summing products associated with the various pathways. One finds that abstraction products represent roughly 35% of the total near 1000 K. The abstraction channels include contributions from radicals other than H atoms, however, so this result indicates only the maximum possible ratio for attack of H atoms on 1-butene. It nonetheless shows that attack of H on 1-butene proceeds predominantly through addition reactions at the temperatures of the present study. This observation is in agreement with experimental¹⁷ and theoretical⁸ results on the related H + propene system.

Literature rate constants indicate that the unimolecular decomposition of 1-butene is slow at our temperatures, as is confirmed by the absence of noticeable loss of this compound. However, because it is present in large excess, even small losses may result in detectable products. Decomposition of 1-butene occurs by fission of the relatively weak allylic C-C bond:

1-butene
$$\rightarrow C_3H_5(allyl) + CH_3$$
 (R28)

Allyl can subsequently expel H to give allene:

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$$allyl \rightarrow allene + H$$
 (R29)

Although allene is observed as a minor product, H ejection is slow at our temperatures because of the allylic resonance energy, and one expects a major loss route of allyl to involve recombination reactions with other prominent radicals in the system.

Radical Recombination Products. Many of the observed minor products result from recombination reactions involving radicals that have no rapid unimolecular modes of decomposition. Such radicals include methyl, allyl, and 1-methylallyl. Also in this category are 3,5-dimethylbenzyl (DMB) radicals formed by abstraction of H from the 135TMB inhibitor:

$$X + 135TMB \rightarrow XH + 3,5$$
-dimethylbenzyl (DMB)
(R30)

We were able to identify by GC/MS most the products from the self-and cross-recombination reactions of the above radicals, except in cases where the resulting compounds are too large to elute in our GC analyses, e.g., DMB + DMB $\rightarrow C_{18}H_{22}$. Routes to some identified products are indicated below; product amounts are tabulated in the Supporting Information if formed at levels greater than 1% of ethene.

$$CH_3 + CH_3 \to C_2H_6 \tag{R31}$$

 $CH_3 + 1$ -methylallyl $\rightarrow 2$ -pentene (*E* and *Z* isomers)

$$CH_3 + 1$$
-methylallyl \rightarrow 3-methyl-1-butene (R33)

(R32)

$$CH_3 + 3.5$$
-dimethylbenzyl(DMB)

$$\rightarrow$$
 3,5-dimethylethylbenzene (R34)

$$allyl + allyl \rightarrow 1,5$$
-hexadiene (R35)

$$\rightarrow$$
 3,5-dimethyl-(3-butenyl)benzene (R36)

allyl + 1-methylallyl \rightarrow 1,5-heptadiene (R37)

$$allyl + ethyl \rightarrow 1$$
-pentene (R38)

While the recombination products indicate the prevalent stable radicals in the system, and thus provide confirmation of the mechanism, these species have little impact on ethene and propene, the olefins used to derive the H atom kinetics of interest.

Reference Reaction for H Atom Kinetics. In the present and previous works we have used reaction R39, the displacement of methyl from 135TMB, as a reference in order to obtain absolute rate constants for attack of H atoms.

$$H + 135TMB \rightarrow m$$
-xylene + CH_3 (R39)

This reaction is the source of the *m*-xylene product. Tsang et al.³⁶ have reported $k(H + 135TMB \rightarrow m$ -xylene + CH₃) = 6.7 × 10¹³ exp(-3255/T) cm³ mol⁻¹ s⁻¹, which in turn is relative to $k(H + CH_4 \rightarrow CH_3 + H_2) = 2.4 \times 10^{11} \exp(-7000/T)$ cm³ mol⁻¹ s⁻¹. In recent work, Sheen et al.³⁷ have reanalyzed the data on the H + propene/135TMB system,¹⁷ applying a detailed chemical kinetic model and spectral uncertainty propagation and minimization techniques. Their analysis suggests parameters for H atom attack on CH₄ and 135TMB that are only slightly different from those given above, with an approximately 10% reduction in the absolute rate constants at

the current temperatures. This is well within the absolute uncertainty factor of about 1.5 suggested by Tsang et al. Because of the minimal difference, and to allow easier comparison with previous work, we retain herein the original parameters of Tsang et al. in the derivation of our rate constants.

Kinetics of 1-Butene Decomposition. Unimolecular decomposition of 1-butene via R28 leads to allyl and methyl radicals. Small amounts of allyl are clearly present in the H atom systems as evidenced by observed recombination products such as 1,5-hexadiene and 3,5-dimethyl-(3-butenyl)benzene, formed via eqs R35 and R36, and the presence of allene formed by eq R29. As a check of our understanding of 1butene decomposition, we have carried out ancillary experiments to examine the pyrolysis of this compound at temperatures higher than utilized in the H atom work. Experiments were conducted at temperatures of 1160 to 1300 K and pressures of 150 to 850 kPa. These experiments (mixture F) utilize very small amounts of 1-butene, approximately 80 μ L/L, in the presence of excess 135TMB as an inhibitor. First order rate constants are derived based on total loss of the substrate, assuming eq R28 to be the operative mechanism.

Additionally, as a consistency check, in the lower temperature H atom experiments with excess 1-butene, where decomposition is minor, we have obtained approximate product-based rate constants for 1-butene decomposition by summing allyl radical equivalents in observed products and making additional approximate corrections for unobserved products, such as the reformation of 1-butene from the reverse of eq R28. Thus, allene, 3,5-dimethyl-(3-butenyl)benzene, 1,5-heptadiene, and 1,5-hexadiene are equivalent to one, one, one, and two allyl radicals, respectively. For the reverse of eq R28, we estimate the 1-butene formed by assuming that the product ratio (allyl + methyl/(allyl + allyl) is equal to that for (DMB + methyl)/ (DMB + allyl). Perhaps more problematic is the potential formation of propene from allyl via H abstraction from 135TMB, disproportionation reactions, or recombination with H atoms:

allyl + 135TMB
$$\rightarrow$$
 propene + DMB (R40)

allyl + H
$$\rightarrow$$
 propene (R41)

$$allyl + RH \rightarrow propene + R$$
 (R42)

One would anticipate these reactions to have low rates, in the case of R40 because of an expected high barrier, for R41 because of low H atom concentrations, and for R42 because of low concentrations of the partner radicals and a general kinetic preference for recombination over disproportionation. Empirically, our data show that propene/ethene ratios are not affected by even a factor of 5 variation in the starting concentration of 1butene. The above reactions can therefore be at most a minor source of propene. With respect to the fate of allyl radicals, we have estimated the conversion to propene in two ways. The first is based on our previous study¹⁸ involving H atom attack on cyclopentane and the decomposition of the pent-4-en-1-yl radical. The latter species decomposes to give allyl + ethene, and allyl is the sole source of propene in that system. Using ethene as the basis of comparison, in the pent-4-en-1-yl system we were able to recover about 90% of the allyl radicals as recombination products or propene. About 12% of allyl radicals were converted to propene based on the propene/ethene ratios.

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An alternate estimate can be made based on the conversion of 1-methylallyl radicals to 2-butenes in the present studies (see previous discussion of 2-butene formation). Derived ratios of (2-butene from methylallyl)/(methylallyl equivalents) were approximately constant for each mixture, and varied between 0.06 and 0.11. The two estimation methods give similar results. In the end we have made our corrections based on 2-butene formation, as this internal method should better account for effects specific to each mixture, e.g., the net impact of variations in the concentration of 135TMB, H atoms, and other radicals. While obviously somewhat crude, our adjustment has only a small effect on our derived rate constants for 1-butene decomposition. Including an estimated 2σ uncertainty of 20 K in our temperatures, we estimate our rate constants based on allyl radical equivalents to have an overall uncertainty factor (2σ) of about 1.7.

The derived rate constants for 1-butene decomposition from our individual experiments are given in the tables in the Supporting Information. Figure 2 summarizes the current shock



Figure 2. Rate constants for 1-butene \rightarrow allyl + CH₃. Static studies include 1950Seh_Szw,³⁸ 1965Kerr_Spe,³⁹ and 1970Trenwith;⁴⁰ the other experimental points are from this work. The dashed and solid lines are respectively the high pressure limit estimated by Dean⁴¹ and the present recommendation.

tube data, together with previous literature results. Previous measurements include those of Sehon and Szwarz,³⁸ who studied 1-butene decomposition between 926 and 1050 K in a flow system using toluene as a carrier to inhibit radical chain decomposition. Kerr et al.³⁹ examined the reaction in a flow system between 900 and 990 K, using aniline as the carrier and inhibitor. Trenwith⁴⁰ employed a static system with no inhibitor, but conducted detailed investigations of surface effects, and was able to make small appropriate corrections. His experiments were carried out at temperatures much lower than the other studies, 689 to 766 K. Rate constants in the above literature investigations were deduced from the initial rates of methane formation, assuming the initial reaction to be R28, fission of the methyl-allyl bond. Also shown in Figure 2 is the 1985 estimate of Dean.⁴¹ Finally, Shibatani and Kinoshita^{42,43} have deduced parameters based on modeling of uninhibited 1butene pyrolysis in a flow system between 829 and 1040 K. Their rate constants, not shown, are a factor of 2 to 3 larger than the other values, but are likely affected by the lack of an inhibitor.

We expect our most reliable results to be from the pyrolysis experiments (mixture F), where rate constants are based on total loss of substrate. In these experiments the shock pressures were varied between 150 and 850 kPa and temperatures were 1160 to 1300 K. Within the scatter we were unable to discern any pressure effects, and a least-squares analysis of these data yields

$$k_{28}/s^{-1} = 10^{15.02 \pm 0.72} \exp[(-34930 \pm 2050) \text{ K/T})$$

(1150-1309 K; 150-850 kPa)

The uncertainties given are 2σ and represent precision only. An extrapolation of 400 K and 7 orders of magnitude in the rate constants yields predictions that are larger than the low temperature results of Trenwith by a factor of 2.2. At the intermediate temperatures, the data from the HME experiments, the studies of Sehon and Szwarz,³⁸ those of Kerr et al.,³⁹ and the above expression all agree within a factor of 2. Agreement with the data from the ethyl iodide experiments is mixed. At the upper end of the covered temperature range the ethyl iodide results coincide with the HME work, but at the lower temperatures where 1-butene conversion is extremely low, rate constants based on allyl equivalents are a factor of 2 to three larger than expected. In part this may reflect difficulties in accurately quantitating the allyl radical products, which were near detection limits at the lower temperatures. Examination of the data also shows, however, that allyl/ethene ratios appear to go through a minimum at about 950 K, which may suggest that small secondary sources of allyl exist at the lower temperatures. At present we ascribe the moderate disagreement to this possibility. The alternative is that the rate constants of Trenwith are far too small, which we consider to be unlikely given that most errors in static studies lead to rate constants that are too large.

A combined treatment of the low temperature results of Trenwith and the high temperature results of the present study leads us to recommend:

$$k_{28}/s^{-1} = 10^{15.53 \pm 0.10} \exp[(-36372 \pm 218) \text{ K/T})$$

(690-1309 K; 150-800 kPa)

This is not a high pressure limiting rate expression, and despite our failure to observe a clear pressure effect, there are likely falloff effects at the upper end of this temperature range. An RRKM analysis could perhaps clarify the situation, but is beyond the scope of the present treatment. The high pressure limit estimate of Dean⁴¹ yields rate constants about a factor of 2 larger than our recommendation. This difference is roughly constant over the entire temperature range, however, even though no significant falloff effects are expected at the lower temperatures. Uncertainties given above are 2σ and represent precision only. Including possible systematic errors, the rate constants from our recommended fit are estimated to have 2σ uncertainties of about 30% at 700 K rising to about 70% at 1300 K. The major uncertainty in the high temperature rate constant is related to the temperature determination. We estimate a 2σ uncertainty of 20 K in the absolute temperatures of our experiments, which translates to uncertainties of about a factor of 3 in the pre-exponential term and 7 kJ mol⁻¹ in the activation energy.

With respect to the H atom studies, the kinetics of 1-butene pyrolysis confirm that its unimolecular decomposition is the source of allyl radicals and that the resulting products are quantitatively in accord with expectations. Decomposition of 1butene is shown to be minor under the conditions of the H atom work and is not expected to significantly interfere with our kinetic measurements of H atom addition.

Kinetics of Displacement Reactions by H Atoms. Terminal and nonterminal addition of H to 1-butene results in displacement of methyl or ethyl radicals and the corresponding formation of propene and ethene via reactions R10–R12. The propene/ethene ratios are thus directly related to the relative displacement rates, assuming that all intermediate radicals decompose and there are no other sources of these species. Our experiments are designed to ensure that these conditions are met, and this is borne out by the detailed analysis of secondary chemistry given below.

Corrections to Ethene and Propene Yields Due to Secondary Chemistry. Before deriving relative and absolute rate constants we have made some minor corrections to the primary data in order to account for secondary chemistry. These corrections are made for completeness, and to demonstrate that possible systematic effects from the secondary chemistry are small. We emphasize, however, that the adjustments ultimately change the results by only about 10%, and do not affect our main conclusions. As our analysis considers all products down to levels of even 1% of the main ethene and propene product olefins, it is highly improbable that we have missed any significant chemistry that would impact our results.

For ethene yields the main concerns are ethyl radicals that may be trapped by recombination reactions prior to decomposition to ethene via eq R12, and any ethene that may result from the decomposition of 3-butenyl radicals (Scheme 1). The main possible trapping radicals for ethyl are methyl, allyl, and DMB, and corrections are applied based on the observed recombination products propane, 1-pentene, and 3,5-dimethylpropyl benzene. Summed, these increase the equivalent ethene yields by only 3-5%. A fraction of the 3butenyl radicals formed by abstraction of H from 1-butene will decompose to ethene and vinyl radicals as shown in Scheme 1. Vinyl will mostly decompose to ethyne + H under our conditions so we can estimate this contribution based on formation of ethyne. In unpublished work we have carried out studies of the reaction H + 1,3-butadiene \rightarrow ethene + C₂H₃, and, based on the observed ratios of ethyne and ethene in that system, have estimated the approximate correction factor to the ethene yield to be 1.5[ethyne]. Ethene amounts attributed to H addition were thus reduced by this amount, typically 3-5%. The contribution to ethene from the chemically activated process $CH_3 + CH_3 \rightarrow C_2H_5 + H$ was also estimated based on the kinetics recommended by Baulch et al.,⁴⁴ but was never more than 0.2%, and so was neglected. For propene, we make two adjustments. First, as discussed in the Experimental Section, a small amount of propene is produced in HME decomposition, and amounts attributed to reaction of H with 1butene are reduced by a quantity equal to $(0.035 \pm$ 0.07)[isobutene], leading to a well-defined correction of typically 2-5%. Second, a small fraction of the allyl radicals produced by 1-butene decomposition are expected to yield propene via eqs R40-R42. Propene yields were consequently reduced based on allyl radical equivalents as previously discussed. This correction is the least certain, but is typically only 5-10%. Empirically, it is certain that the correction is small, as allyl radical production via R28 scales directly with the starting substrate concentration, and a 5-fold variation in the starting 1-butene concentration still results in near-identical propene/ethene ratios, even if no allyl-based adjustment to

propene is made. Further, completely consistent results were obtained from the lower temperature experiments where ethyl iodide was used as the H atom precursor, conditions where 1butene decomposition is negligible and there is no correction to propene from HME decomposition.

Application of the above small adjustments yields the equivalents of ethene and propene that are due to the displacement reactions R10 and R11. The relative rate constants are given by

$$\frac{k_{10}}{k_{11}} = \frac{2[\text{propene}]_{\text{equiv}}}{[\text{ethene}]_{\text{equiv}}}$$

The factor of 2 accounts for the stoichiometry of ethene production. These data are plotted in Figure 3. There are no



Figure 3. Relative rate constants for displacement of methyl and ethyl from 1-butene by H atoms. Values are close to the high pressure limiting ratio of rates for terminal and nonterminal addition of H atoms (see text).

apparent systematic differences for the different mixtures. A combined fit to the data yields

$$\frac{k_{10}}{k_{11}} = 10^{(0.058 \pm 0.059)} \exp[(818 \pm 141) \text{ K/T});$$

971–1120 K

The given uncertainties are 2σ and represent precision only. Additional systematic uncertainties are present due to our small corrections to ethene and propene equivalents. These are manifested primarily in the intercept. Including an additional estimated systematic uncertainty of 8% due to our corrections to ethene and propene equivalents leads to a total estimated uncertainty of $\pm 15\%$.

In a similar fashion, we can derive rate constants relative to the reference reaction of displacement of methyl from 135TMB. Because of their large excess, amounts of 1-butene and 135TMB are essentially unchanged during reaction, leading one to derive:

$$\frac{k_{10}}{k_{39}} = \frac{[\text{propene}]_{\text{equiv}}}{[m-\text{xylene}]} \frac{[135\text{TMB}]_0}{[1-\text{butene}]_0}$$
$$\frac{k_{11}}{k_{39}} = \frac{[\text{ethene}]_{\text{equiv}}}{2[m-\text{xylene}]} \frac{[135\text{TMB}]_0}{[1-\text{butene}]_0}$$

The subscript zeros indicate the starting concentrations. These data are plotted in Figure 4. Arrhenius-type fits to the individual



Figure 4. Rate constants for displacement by H atoms of methyl from 135TMB relative to displacement of methyl and ethyl from 1-butene.

data sets yield very similar slopes, but there are small systematic differences in the intercepts. Systematic differences scale in the same way for ethene and propene, so these are probably due to small errors in the starting 1-butene/135TMB ratios. As noted earlier, propene production and the resulting values of k_{10}/k_{39} obtained with ethyl iodide as the H atom source (Mix D) are in excellent agreement with the HME results. The ethyl iodide experiments yield no reliable information about k_{11} , however, due to the confounding influence of ethene produced by the H atom source.

To fit the data while accounting for the small systematic errors, a least-squares procedure was used to slightly scale the data from each mixture to a common line and the resulting data fit with a standard least-squares analysis. This procedure helps prevent systematic errors in a particular data set from affecting the slope and accounts for differences in the number of experiments performed with each mixture. The resulting fit is

$$\frac{k_{39}}{k_{10}} = 10^{0.232 \pm 0.062} \exp[(-2103 \pm 146) \text{ K/T});$$
880–1120 K

The given uncertainties are 2σ and represent precision only. Including possible systematic errors, the overall uncertainty (2σ) in the relative rate is about ±15%. Employing $k(H + 135TMB \rightarrow m$ -xylene + CH₃) = 6.7 × 10¹³ exp(-3255/T) cm³ mol⁻¹ s⁻¹, for our reference reaction, we derive

$$k_{10} = 3.93 \times 10^{13} \exp(-1152 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1};$$

880–1120 K

And, in conjunction with k_{10}/k_{11}

$$k_{11} = 3.44 \times 10^{13} \exp(-1971 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1};$$

971–1120 K

Uncertainties (2σ) in these absolute rate expressions are about a factor of 1.5 and are due mainly to the uncertainty in the rate of the reference reaction.

4. DISCUSSION

The present results represent the first direct determination of the rates of methyl and ethyl displacement from 1-butene by attack of hydrogen atoms at temperatures near 1000 K. A detailed analysis of products down to the 1% level of the olefins of interest indicates that possible errors from secondary chemistry are small, and thus that the derived branching ratios are of high accuracy. Absolute rate constants have been derived relative to a reference reaction and the main uncertainties are related to the reference rate rather than the relative rate measurements.

The determined phenomenological rate constants apply to composite processes, not true elementary reactions. The butyl radical intermediates are chemically activated and product formation can occur directly or following thermalization. The related case of H + propene has been discussed in detail by Miller and Klippenstein.⁸ In terms of our measured rate constants, the details of the displacement process are of little importance as β -C-C bond scission is the only significant decomposition channel and even the thermalized intermediates have unimolecular lifetimes of less than 1 μ s. Previous work by us^{10,11} and others^{8,15,16} shows that thermal, chemically activated, and tunneling-induced isomerizations will be of minimal importance for butyl radicals under our conditions. The main channel competing with C-C scission is ejection of H and this process should be less than 5% of reaction. The net result is that our measured displacement rate constants should be very close to the high pressure limiting values for terminal and nonterminal addition of H.

Figure 5 shows the results of the more direct measurements of the kinetics of the H + 1-butene reaction. The early



Figure 5. Selected rate constants pertaining to H addition to 1-butene. Circles, triangles, and squares indicate experimental data relevant to the total addition rate constant (k_{tot}), and terminal (k_T), and nonterminal (k_{NT}), addition, respectively. The light and heavy dashed lines represent Arrhenius extrapolations of the present results and the recommended values of Curran.⁹

literature, not presented, has been reviewed by Kerr and Parsonage¹ and is generally consistent with later studies employing more precise techniques. Several researchers^{45–49} have directly measured the total reaction rate at temperatures <440 K by following H atom decay rates in the presence of 1-butene. It is generally argued and accepted that abstraction reactions are unimportant at these temperatures and that addition to the terminal site is the overwhelming process. These conclusions are confirmed by the present results and the recent Miller and Klippenstein⁸ analysis of the analogous H + propene reaction. There are no direct measurements of the rate of nonterminal addition at low temperatures, but studies of

secondary products have been used to deduce the branching ratio between terminal and nonterminal addition and values at 298 K can be derived on this basis. Plotted are the approximate rate constant for nonterminal addition $[k_{\rm NT}(298 \text{ K}) = 5.0 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}]$ as given by Kerr and Parsonage¹ in their 1972 evaluation, and the value derived by us on the basis of the branching ratio data (see below) in conjunction with our preferred value for terminal addition. Also shown in the figure are the recommendations for terminal and nonterminal addition given by Curran⁹ in his 2006 review, in which he adopted identical values for 1-butene and propene. Although a simple Arrhenius extrapolation of our high temperature results leads to good agreement with the lower temperature data down to about 300 K, the data are more consistent with moderate curvature in the addition rate constants.

Branching Ratios for H Addition. The temperature dependence of the site selectivity for H addition is shown in Figure 6. Experimental results are limited, with the only precise



Figure 6. Temperature dependence of the high pressure limit ratio of terminal to nonterminal addition of H to propene and 1-butene. Circles and squares indicate experiment-based data relevant to propene^{5–7} and 1-butene,^{4,7} respectively. The heavy solid line indicates the present results for 1-butene with 2σ error limits. The dotted line is the recommendation of Curran⁹ for both propene and 1-butene, while the light solid line is the 2013 value of Miller and Klippenstein⁸ for propene.

measurement at high temperatures given by the present studies. In good agreement, nonetheless, is the approximate value of 3 (uncertainty not stated) at 923 K derived by Sabatani and Amano⁵⁰ from an analysis of products in 1-butene pyrolysis. At room temperature, Harrington et al.4 studied the decomposition of chemically activated butyl radicals formed by addition of H to 1-butene and reported, on the basis of observed secondary products, that approximately 5% of H atom addition occurs at the nonterminal site near 300 K. In analogous studies of activated propyl radicals, Falconer et al.⁵ arrived at a value of (6 ± 1) % for nonterminal addition of H to propene. Both reports represent ancillary observations, however, and neither work provides the primary data or specifics of the analysis. More comprehensive studies were subsequently reported by Falconer and Sunder⁷ in 1971 and Wagner and Zellner⁶ in 1972. Falconer and Sunder investigated the orientation of H addition to both propene and 1-butene at 298 K and pressures of (25 to 700) torr [(3.3 to 93.3) kPa]. They generated H atoms via mercury-photosensitized decomposition of H₂ and used GC methods to determine ratios of the recombination products of the isomeric adduct radicals. After

applying corrections for disproportionation/combination ratios, they derived the percentages of nonterminal addition to be 5.7 \pm 0.1 for propene and 5.7 \pm 0.14 for 1-butene, where the uncertainties represent precision only. Similar results were obtained by Wagner and Zellner,⁶ who employed a flow reactor together with a microwave discharge system for H atom production and GC/MS analytical techniques to investigate the stable products of H atom addition to propene at temperatures of 190 to 390 K and pressures of 1.6-20 Torr (0.21-2.7 kPa). For addition of H at 300 K, they derive $k_{\text{nonterminal}}/k_{\text{terminal}} =$ 0.068, which corresponds to 6.4% addition at the nonterminal site (uncertainties are not given, but have been assumed by us to be approximately 15% at the 2σ level of confidence). Figure 6 also includes lines indicating the estimates of Curran,^{9°} the present recommendations for 1-butene, and the high pressure limiting values for propene given by Miller and Klippenstein.⁸ Curran⁹ recommends identical values for propene and 1-butene and his branching ratios are about 35% larger than the present measurements near 1000 K. Probably the most striking observation is the factor of 3 disparity between the present results and the recent values of Miller and Klippenstein for propene, which are based on high-level computational chemistry results that have been slightly tuned to fit a variety of experimental observations. This is discussed in greater detail below, but we think it unlikely that there are large rate differences between propene and 1-butene, thus suggesting that there remain inconsistencies in current models of the H + propene reaction.

Recommended High Pressure Rate Expressions. We have derived recommended high pressure rate expressions for addition of H to 1-butene over an extended temperature range using the following procedure. For the total addition rate constant at 300 K, we have taken an average of the direct measurements by Oka and Cvetanovic,46 Harris and Pitts, and Kyogotu et al.⁴⁷ and arrive at $k_{\text{total}}(300 \text{ K}) = (1.04 \pm 0.25) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, where the uncertainty is 2σ and includes our estimate of systematic errors. The best measurement of the branching ratio for terminal and nonterminal addition of H to 1-butene at low temperatures appears to be that of Falconer and Sunder.⁷ They obtained identical values for 1-butene and propene, and their value for propene agrees with that of Wagner and Zellner⁶ within 12%. We have adopted at 300 K the value $k_{11}/k_{10} = k_{\text{nonterminal}}/k_{\text{terminal}} = (0.060 \pm 0.009)$, where the overall uncertainty (2σ) , including systematic errors, has been estimated by us to be 15%. This value is quite similar to other recommendations (see Figure 6). Combined with the present high temperature results, an Arrhenius fit yields

$$\frac{k_{10}}{k_{11}} = 10^{(0.068 \pm 0.010)} \exp(795 \pm 22 \text{ K/T}); \ 300 - 1120 \text{ K}$$

The uncertainties given in this expression are 2σ and represent precision only. Absolute uncertainties are about $\pm 15\%$ over this range of temperatures. With this expression in hand, the temperature dependent measurements of k_{total} by Harris and Pitts, and Kyogotu et al. were then each scaled slightly by an appropriate constant so as to match our preferred value of $k_{\text{total}}(300 \text{ K})$, and then split into terminal and nonterminal components based on the above equation. These data were combined with the present high temperature measurements and fit with modified Arrhenius equations of the form AT^n $\exp(-E/T)$, yielding the fits shown in Figure 7. The rate expressions are



Figure 7. High pressure rate expressions for terminal and nonterminal addition of H to 1-butene. Experimental results for k(total) at low temperatures^{45,47} have been scaled and split into components as discussed in text. Dotted lines show the 2006 recommendations of Curran;⁹ dashed lines are the 2013 values of Miller and Klippenstein⁸ for propene; heavy and light solid lines indicate the present experimental data and recommended fits, respectively.

$$k_T = 1.05 \times 10^9 T^{1.40} \exp(-366 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

 $k_{NT} = 9.02 \times 10^8 T^{1.40} \exp(-1162 \text{ K/T}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

These rate expressions refer to the high pressure limiting values for H atom addition to the terminal $(k_{\rm T})$ and nonterminal $(k_{\rm NT})$ positions and are recommended from 220 to 2000 K. Absolute uncertainties (2σ) in these rate constants are estimated to be $\pm 25\%$ at 300 K, rising to $\pm 50\%$ at 1000 K and a factor of 2 at 2000 K.

Implications for Propene and Other 1-Olefins. At low temperatures, when comparing results by the same researcher using a single technique, rates of H atom addition appear to be very similar for all normal 1-olefins. For instance, in multiple studies by a variety of direct⁴⁵⁻⁴⁹ and relative rate⁵¹⁻⁵³ techniques, and at temperatures of 220-440 K, propene and 1-butene are generally found to have rates equal to within about 15%, and differences are not clearly distinguishable from experimental scatter. Data on larger species are limited, but Cvetanovic and Doyle⁵² found only a 10% rate difference between propene and 1-pentene at room temperature. As noted previously, these low temperature results pertain predominantly to terminal addition of H. At high temperatures, we have in this laboratory previously derived methyl displacement rates for propene¹⁷ (corresponding to nonterminal addition) using the same 135TMB standard employed here. Comparison of these data with the present results suggests that, near 1000 K, nonterminal addition of H to propene is about 15% faster than nonterminal addition to 1-butene. This difference may be real, but is close to our experimental ability to discern. A visual comparison of literature results for propene and 1-butene is provided in Figure S1 of the Supporting Information. The overall conclusions are that the relative and absolute rates of terminal and nonterminal addition are very similar for propene and 1-butene, and that the presently determined addition rates should be generally applicable to unbranched 1-olefins with minimal error. Note that these rates should not be applied to 1olefins such as isobutene that have branching at the double bond position. We lack direct information on the impact of branching removed from the double bond position, but this will likely have minimal effects.

The disparity with the Miller and Klippenstein result for propene (Figure 6) is somewhat troubling. In their modeling of propyl radical dissociation and other reactions on the C_3H_7 potential energy surface Miller and Klippenstein obtained good fits to a variety of experimental data, including results on addition of H to propene at low temperatures, displacement of methyl from propene by H atoms, and dissociation of propyl radicals. Despite this, the model does not reproduce the present data.

In their analysis, Miller and Klippenstein provide rate constants for the chemically activated displacement process, H + propene \rightarrow *n*-propyl^{*} \rightarrow ethene + CH₃, and distinguish these from the production of thermalized *n*-propyl: H + propene \rightarrow *n*-propyl* \rightarrow *n*-propyl. They compare their modeled pressure-dependent rate constants for chemically activated displacement with phenomenological values for displacement of methyl from propene as determined previously in this laboratory.¹⁷ Although good agreement is found, the rate constants determined in the shock tube studies apply to the sum of the chemically activated and thermal decomposition processes. We suggest a better comparison is probably with their high pressure limiting rate constants for nonterminal addition (the total capture rate constants), although that comparison is also not perfect, as it fails to account for the admittedly minor fraction of species that undergo C-H bond scission or isomerization. As it happens, under the studied conditions the different approaches result in only modest differences (approximately 15%) in the derived rate constants. This is insufficient to resolve the problem.

Our suspicion is that the issue may involve the rate constants for terminal addition (see Figure 7), but adjustments there would obviously impact the reverse *i*-propyl radical dissociation rates, where the model shows good agreement with experimental data. It remains to be seen if acceptable fits to all data could be recovered with appropriate adjustments to, e.g., barriers to reaction, thermochemistry, and the tunneling and energy transfer parameters.

The impact of the above on combustion models will vary with the temperature. Under many conditions terminal addition of H to propene is simply reversed, and so errors in this rate constant will have minimal effects unless they are rooted in problems with the thermochemistry and derived radical equilibriums. The main issues will arise at temperatures where propyl radicals are moderately stable and bimolecular reactions are competitive with decomposition. In this regime errors in the branching ratio will lead to erroneous concentrations of the n-propyl and isopropyl forms. Note that the reversal of terminal addition of H at higher temperatures applies only to the propene case. Other 1-olefins form radicals that will undergo decomposition via C-C bond scission reactions. This will lead to particular problems if the branching ratios of reference 8 for propene are applied as reference values in the extrapolation to other systems, e.g. via rate rules or automated mechanism generation techniques. The present values are expected to be more reliable for such purposes.

5. SUMMARY AND CONCLUSIONS

In the current work shock tube methods have been used to thermally generate hydrogen atoms and investigate their reactions with 1-butene at temperatures of 880–1120 K and pressures of 145–245 kPa. Relative and absolute rate constants for displacement of methyl and ethyl by H atoms have been determined and related to the high pressure rate constants for hydrogen atom addition to the terminal and nonterminal positions of the olefin. Addition to the terminal site is favored by a factor of 2.59 ± 0.39 at 1000 K.

The present results have been combined with data from studies at temperatures <440 K and used to derive recommended high pressure rate expressions for H atom addition to 1-butene at temperatures of 220-2000 K. These expressions should also closely approximate the behavior of other unbranched 1-olefins and can reliably be used as estimates for unstudied 1-olefins in detailed kinetic models of combustion and pyrolysis. A factor of 3 discrepancy in the branching ratio for terminal and nonterminal addition is noted when comparing the present experimental results with a recent comprehensive analysis and theoretical modeling study of the important H + propene reaction. It is suggested that the difference is well outside of the possible experimental errors of the present study or the expected differences with 1-butene. Inconsistencies in the H + propene model thus remain and we do not recommend extrapolation of the addition branching ratios in that model to other systems.

ASSOCIATED CONTENT

S Supporting Information

Product data from mixtures A through E on species present at levels >1% of ethene, rate constants derived from individual experiments, and a figure showing the similarity of the literature rate constants for H atom addition to propene and 1-butene. This material is available free of charge via the Internet at http://pubs.acs.org.

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